PATENT 1422-0511P

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

| | | |
|---|---|---|
| In Re Application of | : | |
| Kazuo OKI et al. | : | Group Art Unit: 1751 |
| Serial No.: 10/020,166 | : | |
| Filed: December 18, 2001 | : | Examiner: BOYER, Charles I |

For: BASE PARTICLES AND DETERGENT PARTICLES

# DECLARATION UNDER 37 C.F.R. 1.132

HONORABLE COMMISSIONER OF
PATENTS & TRADEMARKS
WASHINGTON, D.C. 20231

Sir:

I, Kazuo OKI, residing in Wakayama-shi, Wakayama-ken, Japan, hereby declares and states as follows:

1. That I am one of the co-inventors of U.S. Application Serial No. 10/020,166 filed on December 18, 2001, entitled BASE PARTICLES AND DETERGENT PARTICLES. I am thoroughly familiar with the contents of said Application, its prosecution before the United States Patent and Trademark Office and the references cited therein.

2. That I am a graduate of Saitama University, Faculty of Engineering in the year 1990, majoring in applied chemistry.

3. That I have been employed in Kao Corporation in the year 1990 and have been assigned to the Research Laboratories.

4. That I have been involved in the research and development of material science since 1990.

5. That the following experiments were conducted by myself or under my direct supervision and control in order to verify that the zeolite of the present invention has completely different aggregate particle size distribution and cationic exchange capacity from those of zeolites disclosed in WO 00/18872 and those of conventionally known, commercially available zeolite.

ZEOLITES

As zeolites of Reference Examples I to III, of the zeolites described on page 24, lines 3-13 and Table 2 of WO 00/18872, Zeolite P commercially available from Crossfield under the trade name of Zeolite MAP was used as Reference Example I, Zeolite X commercially available from Degussa under the trade name of Wessalith XD was used as Reference Example II, and Zeolite 4A commercially available from Wako Pure Chemical Industries under the trade name of Zeolite, Synthetic, A-4 was used as Reference Example III. The properties of the resulting zeolites are shown in Table A.

As the inventive products, those zeolites prepared by the methods described in Examples 1 to 3 of the present specification were used. Specifically, these zeolites were prepared as follows.

Example 1

Zeolite was prepared by the following method, using a mixer-synthesizer schematically shown in Figure I, which comprises a reaction tank 3 (350-L stainless tank) equipped with an external circulating line 6 having a mixer 5. In

the mixer-synthesizer, a liquid can be conveyed to the circulating line 6 with a liquid-conveying pump 2 (commercially available from DAIDO METAL CO. LTD., WP pump, Model: WP3WL140C0) from the bottom of the reaction tank 3, and raw materials can be fed to a position immediately before the inlet of the mixer 5 (line mixer; commercially available from Tokushu Kika Kogyo Co. Ltd., Model: 2S6) via a raw material feed line 7 from a raw material tank 1 (200-L stainless tank).

The amount 105.6 kg of an aqueous solution of No. 3 water glass ($Na_2O$: 9.68% by weight, $SiO_2$: 29.83% by weight) was placed in the raw material tank 1, and stirred at a stirring rate of 100 rpm with agitation impellers 8 having a length of 210 mm. Then, 28.3 kg of a 48% by weight aqueous sodium hydroxide was supplied to the tank, and 72.2 kg of a 0.81% by weight aqueous calcium chloride was further supplied thereto. The resulting mixture was heated to 50°C. Next, 95.0 kg of an aqueous sodium aluminate ($Na_2O$: 21.01% by weight, $Al_2O_3$: 28.18% by weight) was supplied to a reaction tank 3, and heated to 50°C, with stirring at a stirring rate of 100 rpm with an agitator 4 comprising one each of a pitch paddle (not shown in the figure) and an anchor paddle (not shown in the figure), each having a length of 500 mm. While the aqueous sodium aluminate was circulated in advance to the circulating line 6 at a flow rate of 40 kg/min (linear velocity of the circulating line: 0.35 m/s) with the liquid-conveying pump 2, with operating the agitator 4, the reaction was initiated by setting the rotational speed of the mixer 5 at 3600 rpm (peripheral speed of the turbine: 16 m/s), and feeding the solution in the raw material tank 1 into the circulating line 6 via the raw material feed line 7. After the termination of the reaction (after the addition of the entire raw material in the raw material tank 1), the raw material had a

compositional ratio such that an $SiO_2/Al_2O_3$ molar ratio was 2, that an $Na_2O/Al_2O_3$ molar ratio was 2.5, and that $CaO/Al_2O_3$ molar ratio was 0.02. the liquid-conveying pump 2 was adjusted so that the circulation flow rate was 130 kg/min (linear velocity of the circulating line: 1.5 m/s). The temperature was raised to 80°C, while the slurry obtained by the reaction was circulated, and the mixture was aged for 60 minutes with keeping the temperature at 80°C.

The resulting slurry was taken out of the above mixer-synthesizer, filtered and washed until the pH of the filtrate attained to 11.4. The resulting residue was dried at 100°C for 13 hours, to give a zeolite powder.

X-ray diffraction patterns of the resulting zeolite were measured using an X-ray diffractometer (commercially available from K.K. Rigaku, Model: RINT2500VPC) under the conditions of CuK $\alpha$-ray, 40 kV, and 120 mA. The zeolite was qualitatively evaluated based on the diffraction patterns presented in JCPDS. As a result, the zeolite was found to be zeolite 4A-type. The resulting zeolite had a composition of $1.02Na_2O \bullet 2.05SiO_2 \bullet Al_2O_3 \bullet 0.02CaO$.

In addition, an SEM image of the resulting zeolite powder was photographed at a magnification of 1000 using an SEM. Thereafter, the distribution of the aggregate particle diameter determined using the SEM image. The properties of the resulting zeolite are shown in Table A.

<u>Example 2</u>

The zeolite obtained in Example 1 was classified by the following method. Thirty-five kilograms of an aqueous solution containing the zeolite at a concentration of 20% by weight was placed in a cylindrical stainless container (inner diameter: 400 mm, height: 300 mm). The zeolite was homogeneously

stirred and dispersed, and thereafter the solution was allowed to stand at 20°C for 12 hours. As a result, precipitates in a volume with a height of 70 mm from the bottom, and supernatant in a volume with a height of 230 mm in the container were obtained. After removing the supernatant by decantation, the zeolite precipitation was obtained. A 100 g portion of the obtained zeolite was placed in a 500-mL beaker, and dried at 100°C for 13 hours. Thereafter, the distribution of the aggregate particle diameter was determined in the same manner as in Example 1. The properties of the resulting zeolite are shown in Table A.

<u>Example 3</u>

The zeolite obtained in Example 1 was pulverized by the following method. Five-hundred grams of an aqueous solution containing the zeolite at a concentration of 40% by weight was placed in a 1-L polystyrene sealed container together with 2000 g of zirconia ball having a diameter of 5 mm. Pulverization was carried out in a ball-mill (300 rpm) for 12 hours, and a 100 g portion of the resulting slurry was placed in a 500-mL beaker and dried at 100°C for 13 hours. Thereafter, the distribution of the aggregate particle diameter was determined in the same manner as in Example 1. The properties of the resulting zeolite are shown in Table A.

<u>TESTING METHODS</u>

Each of the zeolites obtained above was evaluated for its aggregate particle size distribution and cationic exchange capacity. Specifically, average primary particle diameter, average aggregate particle diameter, standard

deviation, variation coefficient, and cationic exchange capacity were evaluated as follows.

(1) Primary Particle Diameter

The longest width of each of 50 or more particles, each being confirmed to be a single particle (region encircled by a smaller circle in Figure II), based on an SEM image of zeolite photographed at a magnification of 5000 by a scanning electron microscope (commercially available from Shimadzu Corporation, SUPERSCAN-220, hereinafter the same) was measured by using a digitizer (commercially available from GraphtEc CORPORATION, "DIGITIZER KW3300," hereinafter the same). The average value of the found values obtained was defined as a primary particle diameter.

(2) Average Aggregate Particle Diameter and Variation Coefficient of Distribution of Aggregate Particle Diameter

In an SEM image (for instance, Figure III) of the zeolite photographed at a magnification of 1000 using a scanning electron microscope, an aggregate of primary particles (region encircled by a larger circle in Figure II) was defined as aggregated particles, and the largest diameter of the aggregated particles was measured by the digitizer. The number-based average value of the particle diameters of 50 or more aggregated particles obtained was defined as an average aggregate particle diameter (D). In addition, the standard deviation ($\sigma$) was calculated from the distribution of the particle diameter of the aggregated particles, and the value calculated from the expression:

Standard Deviation ($\sigma$) $\div$ Average Aggregate Particle Diameter (D) $\times$ 100

was defined as variation coefficient (unit: %).

(3) Cationic Exchange Capacity of Zeolite

One-hundred milliliters of an aqueous calcium chloride (100 ppm, when calculated as $CaCO_3$) at 10°C is added to a 100 mL beaker, and stirred at a rotational speed of 400 r/min with a stirrer piece of 30 mm × 8 mm. Next, a sample is accurately weighed (0.04 g in a case where the zeolite is a powder, and 0.04 g of zeolite calculated on a solid basis in a case where the zeolite is in an aqueous slurry state), and supplied to the aqueous calcium chloride under stirring. After stirring the mixture at 10°C for a given time period (1 minute or 10 minutes), the mixture is filtered with a membrane filter with 0.2 μm pore size. Ten milliliters of the filtrate is taken and assayed for Ca content in the filtrate by an EDTA titration, and the amount of Ca (when calculated as $CaCO_3$) ion-exchanged by 1 g of the sample after 1 minute or 10 minutes is calculated by the following equation, and defined as cationic exchange capacity of zeolite after 1 minute or 10 minutes.

Cationic exchange capacity of zeolite after 1 minute or 10 minutes

$$= ((B - V) \times M \times 100.09 \times 100/10)/S$$

wherein:

B: EDTA titer (mL) for the blank (calcium chloride solution (100 ppm, when calculated as $CaCO_3$))

V: EDTA titer for a sample solution (mL)

M: Molar concentration of EDTA (mol/L)

100.09: Molecular weight of $CaCO_3$ (g)

100: Amount of the calcium chloride solution used for the measurement (mL)

10: Amount of a solution to be titrated (mL)

S: Amount of zeolite powder (g)

## RESULTS AND DISCUSSION

The results are shown in Table A.

Table A

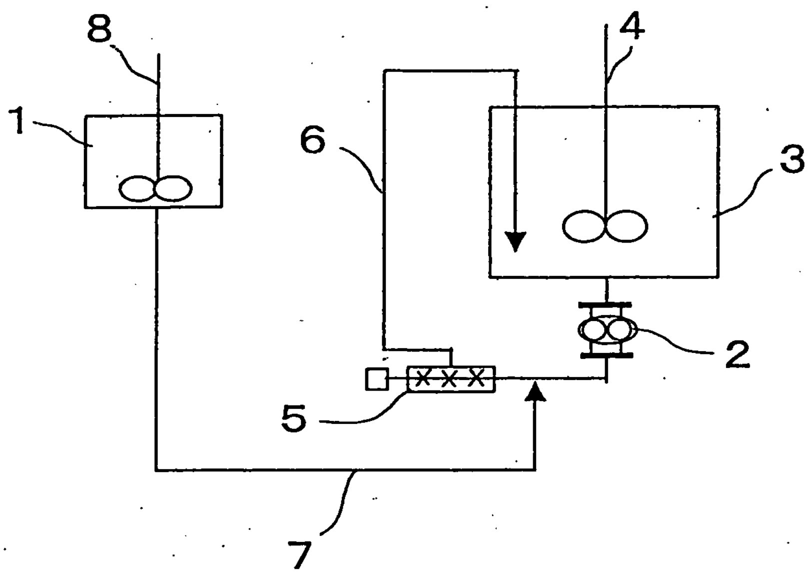
| | Primary Particle Size | Aggregate Particle Diameter | | | Cationic Exchange Capacity of Zeolite Itself | | Crystal Form |
|---|---|---|---|---|---|---|---|
| | Average Primary Particle Diameter (μm) | Average Aggregate Particle Diameter (μm) | Standard Deviation (μm) | Variation Coefficient (%) | Cationic Exchange Capacity After 1 Minute (mg $CaCO_3$/g) | Cationic Exchange Capacity After 10 Minutes (mg $CaCO_3$/g) | |
| Ex. 1 | 0.8 | 6.60 | 1.85 | 28.0 | 196 | 221 | 4A |
| Ex. 2 | 0.8 | 8.07 | 1.76 | 21.8 | 208 | 229 | 4A |
| Ex. 3 | 0.8 | 0.88 | 0.11 | 12.5 | 217 | 229 | 4A |
| Ref. Ex. I | 0.5 | 5.00 | 3.11 | 62.2 | 75 | 123 | P |
| Ref. Ex. II | 0.4 | 6.36 | 3.42 | 53.8 | 147 | 159 | X |
| Ref. Ex. III | 1.8 | 5.45 | 2.75 | 50.5 | 116 | 185 | 4A |

Note: Ref. Ex. I: Zeolite P commercially available from Crossfield under the trade name of Zeolite MAP
Ref. Ex. II: Zeolite X commercially available from Degussa under the trade name of Wessalith XD
Ref. Ex. III: Zeolite 4A commercially available from Wako Pure Chemical Industries under the trade name of Zeolite, Synthetic, A-4

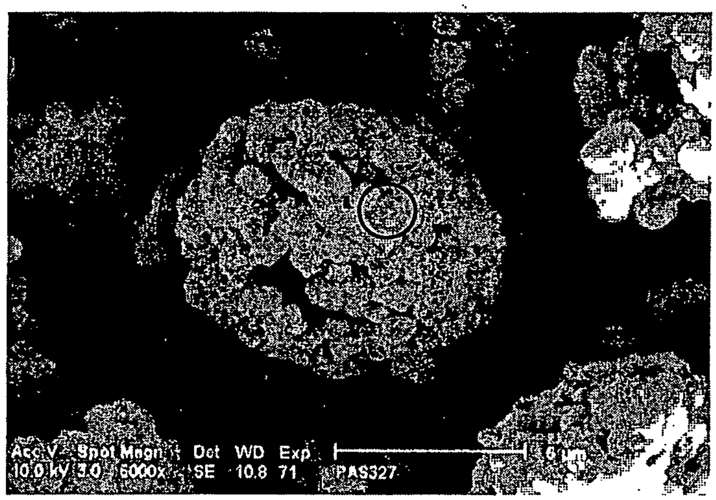
It can be seen from the above results that all of the aggregate particle size distribution of the zeolites disclosed in WO 00/18872 do not fall under the range as defined in claim 1 of the present invention (an average aggregate particle diameter being 15 μm or less and a variation coefficient of a distribution of an aggregate particle diameter being 29% or less). Therefore, these zeolites disclosed in WO 00/18872 are clearly different from those zeolites used in the present invention.

Also, it can be seen that all of the zeolites disclosed in WO 00/18872 have significantly lower cationic exchange capacity as compared to those zeolites prepared in the present invention.

FIG. I

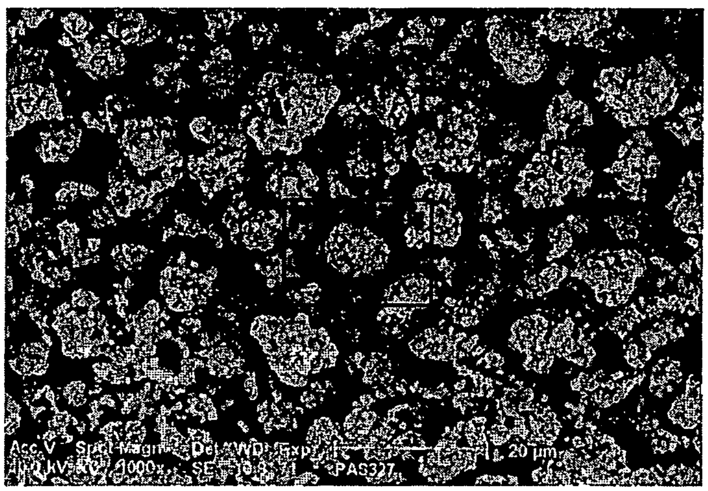


# FIG. II




5 μm

# FIG. III




20 μm

6. The undersigned petitioner declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

7. Further declarant saith not.

Kazuo Oki

Kazuo OKI

September 2, 2004

Date